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Cahn–Hoffman ξ-Vector and Its Relation to Diffuse Interface Models of Phase Transitions

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In this paper we review two important theoretical areas to which J. W. Cahn has made major contributions: (i) The theory of the ξ-vector developed by Hoffman and Cahn, which provides an elegant setting for the description of the equilibrium shapes of sharp interfaces in the presence of anisotropic surface energy. (ii) Diffuse interface theories of phase transitions. We describe recent work which connects these two complementary facets of models of interfaces by the development of a generalized ξ-vector for diffuse interface models with anisotropic surface energy. We show that the generalized ξ-vector plays a central role in both the mathematical and physical aspects of a wide range of diffuse interface theories of interfaces with either anisotropic surface energy or attachment kinetics.

KEY WORDS: Anisotropy; surface energy; diffuse interface model; phase-field model; stress tensor; equilibrium shapes.

1. INTRODUCTION

In this paper we review recent developments that combine two of areas of research to which J. W. Cahn has made important contributions; diffuse interface theory of interfaces and the ξ-vector for the description of interfacial surfaces with anisotropic surface energy. We show how a connection can be made between anisotropic diffuse interface models of interfaces and the ξ-vector formalism by a natural generalization of the ξ-vector originally conceived by Hoffman and Cahn(1, 2) for sharp interfaces. We show that the generalized ξ-vector plays a central role in the theory of anisotropic diffuse interface models from describing the equilibrium interface shape, to representing the entropy flux of a moving interface, as well as describing

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the notion of stress in the interface through its role in contributing to the reversible part of the stress tensor.

Up until the end of the nineteenth century interfaces were mainly considered to be surfaces in what is often termed a "sharp interface" or "free-boundary problem" description. In this formulation an interface is attributed physical properties different from the bulk phases that it separates, e.g., surface energy, γ, is given as an energy excess per unit area. It was in this setting that interfaces with anisotropic surface energy were discussed and, in particular, their equilibrium shapes studied.

The equilibrium shape of an isothermal interface of a pure material may be found by minimising the total energy of the system which is comprised of the energy of the interface due to its surface energy plus the energy of each of the bulk phases, subject to the constraint that the volume enclosed by the interface is constant. A simple calculation gives that

$$\gamma \mathscr{K} = -\Delta f \tag{1}$$

Here $\mathscr{K}$ is the mean curvature of the interface and Δf is the free energy difference (per unit volume) between the two interfaces given by $L(T-T_M)/T_M$, where T is the temperature of the system, T_M the melting temperature of a planar interface, and L the latent heat per unit volume. Equation (1) may be expressed as

$$T = T_M - \gamma \frac{T_M}{L} \mathscr{K} \tag{2}$$

the so-called Gibbs–Thomson equation. It is satisfied in two dimensions by a circular interface shape.

When the surface energy is anisotropic the same procedure in two dimensions gives that

$$T = T_M - [\gamma(\theta) + \gamma''(\theta)] \frac{T_M}{L} \mathscr{K} \tag{3}$$

where θ is the angle subtended by the normal to the interface with a fixed direction.

In three dimensions this procedure results in a much more complicated formula, and is best described compactly by adopting the Hoffman–Cahn ξ-vector as we describe in the next section.

The description of equilibrium shapes of interfaces with anisotropic surface energy dates back to the Gibbs–Wulff construction$^{(3,4)}$ which describes a geometric procedure to determine the equilibrium shape based upon the γ-plot; a polar plot in which $r \equiv \gamma(\vec{e}_r)$, where $\vec{e}_r$ is the unit radial vector. A review of this classical area of theory is given by Frank(5) and Mullins.(6) The Cahn–Hoffman ξ-vector theory developed in the 1970's encompasses these ideas and places them in an elegant and relatively simple framework.

In contrast to sharp interface models, diffuse interface theories recognise that in reality the interfaces have a small, but finite, thickness in which physical quantities vary between their values in the bulk phases. Quantities in the sharp interface formulation which are viewed as localised in the interfacial surface are, in the diffuse interface treatment, identified as being distributed throughout the interfacial region. For example, the surface energy of the interface is derived from the raised Helmholtz free energy density associated within the interfacial region.

Diffuse interface models are based on a thermodynamics involving gradients of the thermodynamic variables to account for nonlocal effects. Originally they were developed to investigate liquids near their critical point and have subsequently been refined and developed to account for a wide range of physical situations such as liquid crystals,(7) spinodal decomposition(8, 9) and ordering transitions in alloys.(10–12) Rowlinson and Widom(13) give a detailed account of their historic development.

In this paper we briefly review both the Cahn–Hoffman ξ-vector and diffuse interface theories of interfaces. In particular, we discuss recent developments which allow diffuse interface models to describe interfaces with anisotropic surface energy. Subsequently, we show how these two complementary approaches may be unified by a generalised Cahn–Hoffman ξ-vector. We go on to describe its use in a range of different diffuse interface models associated with both solid–liquid and solid–solid phase transitions. We illustrate its utility in the context of anisotropic phase-field models of solid–liquid interfaces where it may be used in their sharp interface asymptotic analysis, determination of the type of their partial differential equations, as well as contributing to both the entropy flux and reversible part of the stress tensor that emerges in the derivation of the phase-field model in the setting of irreversible thermodynamics. Finally, we illustrate the use of the ξ-vector in the analysis of anisotropic wavefronts of which kinetically driven crystal growth is a particular example.

2. CAHN–HOFFMAN ξ-VECTOR

Hoffman and Cahn(1, 2) developed the ξ-vector to describe surface energy anisotropy in a first order phase transition represented by a sharp interface. The orientation of a surface element may be characterized in terms of its local normal unit vector, $\vec{n}$, or equivalently by the spherical coordinates θ and ϕ that define the radial unit vector $\vec{e}_r = \vec{n}$. If the surface energy is then written in the form $\gamma = \gamma(\theta, \phi)$, Hoffman and Cahn defined the ξ-vector by

$$\vec{\xi} = \nabla[r\gamma(\theta, \phi)] = \gamma\vec{e}_r + \gamma_\theta\vec{e}_\theta + \frac{1}{\sin\theta}\gamma_\phi\vec{e}_\phi \tag{4}$$

where $\vec{e}_\theta$ and $\vec{e}_\phi$ are unit vectors tangent to the interface in the direction of θ and ϕ increasing, respectively. In the isotropic case (constant γ), the ξ-vector reduces to the form $\vec{\xi} = \gamma\vec{n}$. From the above definition it follows that ξ-vector is in the direction of the normal to the $1/\gamma$-plot defined by $r = 1/\gamma(\theta, \phi)$ and that

$$\vec{\xi} \cdot \vec{n} = \gamma(\vec{n}) \tag{5}$$

which provides a geometric interpretation of the ξ-vector in relation to the geometry of the $1/\gamma$ surface which we illustrate in Fig. 1 for the two dimensional case.

Hoffman and Cahn showed that the interface satisfies the condition

$$\nabla_S \cdot \vec{\xi} = -\Delta f \tag{6}$$

where $\nabla_S \cdot$ is the surface divergence on the interfacial surface, S, and Δf is the bulk free-energy difference across the interface. The corresponding

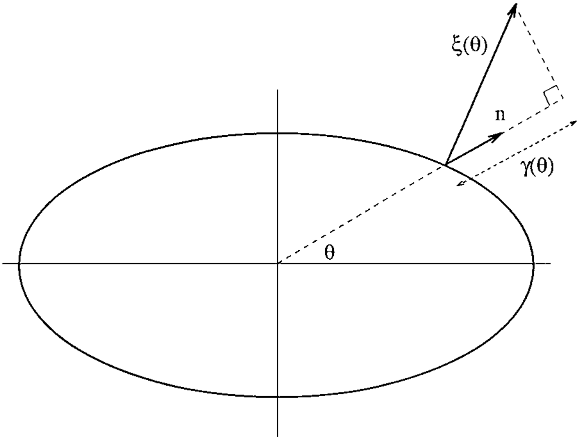

Fig. 1. A schematic diagram of the relation of the ξ-vector to the $1/\gamma$-plot in two dimensions. The solid curve shows the $1/\gamma$-plot for a surface energy with two-fold anisotropy. The ξ-vector is normal to the $1/\gamma$-plot. It follows from Eq. (5) that the projection of ξ-vector onto the normal $\vec{n}$ of the $1/\gamma$-plot is $\gamma(\theta)$.

Gibbs–Thomson equation for an anisotropic surface energy may be written in the form

$$T = T_M - \frac{T_M}{L} \nabla_S \cdot \vec{\xi} \tag{7}$$

where T is the local interface temperature, T_M is the melting point, and L is the latent heat of fusion per unit volume. They went on to show that the equilibrium shapes are given by $\vec{x} = -2\vec{\xi}/\Delta f$, i.e., the envelope of the ξ-vectors, and that this is equivalent to the Gibbs–Wulff construction. If the surface energy anisotropy is so pronounced that the $1/\gamma$-plot is not convex, they showed that corners form in the equilibrium shape, and in two space dimensions they demonstrated that the ξ-vector is continuous across corners. In fact in this situation the ξ-vector plot develops "ears" and the equilibrium shape is formed from its interior envelope, see Fig. 2. The intimate relation between the $1/\gamma$-plot and the equilibrium shape (revealed here by the $\vec{\xi}$-vector) is discussed by Frank$^{(5)}$ who shows that they are dual to one another.

Cahn and Hoffman also showed that the force, $d\vec{f}$, acting on a line element $d\vec{l}$ in the interface is given by

$$d\vec{f} = \vec{\xi} \times d\vec{l} \tag{8}$$

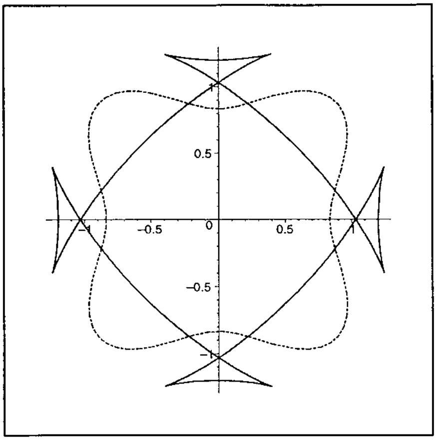

Fig. 2. The solid curve is the ξ-vector plot and the dashed curve is the $1/\gamma$-plot for $\gamma(\theta) \propto 1 + 0.2 \cos 4\theta$. For this case the $1/\gamma$-plot is not convex and the ξ-vector plot forms "ears." The equilibrium shape is given by the interior envelope of the ξ-vector plot; in this case it exhibits four corners.

Consequently the continuity of the ξ-vector at a two-dimensional corner represents a force balance. In the case of a multijunction where n interfaces intersect along a curve, $\mathscr{C}$, they showed that the force balance is given by

$$\sum_{k=1}^{k=n} \vec{\xi}_k \times \vec{l} = 0 \tag{9}$$

where $\vec{\xi}_k$ is the kth interface at the multijunction and $\vec{l}$ is the unit tangent vector to $\mathscr{C}$. For the case of isotropic surface energies this reduces to Young's Law.

More recently Taylor$^{(14)}$ stated an equivalent definition of the ξ-vector by employing a homogeneous extension of degree one of $\gamma(\vec{n})$, where $\vec{n}$ denotes a unit normal, to arbitrary non-zero vectors $\vec{p}$ by

$$\gamma(\vec{p}) = |\vec{p}|\, \gamma(\vec{p}/|\vec{p}|) \tag{10}$$

She showed that the cartesian components of ξ-vector may be defined by

$$\xi^j = \frac{\partial \gamma(\vec{p})}{\partial p_j} \tag{11}$$

It follows from this definition that the ξ-vector is a homogeneous function of degree zero, and that

$$\gamma(\vec{p}) = \vec{p} \cdot \vec{\xi}(\vec{p}), \qquad d\gamma = \vec{\xi} \cdot d\vec{p}, \qquad \vec{p} \cdot d\vec{\xi} = 0 \tag{12}$$

which are properties of the ξ-vector noted by Hoffman and Cahn, for the case when $\vec{p}$ represents the unit normal to the interface.

3. DIFFUSE INTERFACE MODELS

3.1. Isotropic

Diffuse interface models of phase transitions date from Rayleigh$^{(15)}$ and van der Waals$^{(16)}$ who developed such a model for a fluid near its critical point; a situation in which the interface thickness increases as the critical temperature is approached. Subsequently, related theories based on square gradient energy functionals, so-called Landau–Ginzburg theories, have been applied to a wide range of phase transitions. Halperin, Hohenburg and Ma$^{(17)}$ provided a classification of them. Below we briefly review this theory for some particular phase transitions.

3.1.1. Critical Fluid. In the case of a liquid in equilibrium with its gas the density, ρ, may be used to characterise the state of the fluid. An isothermal fluid near its critical point has a Helmholtz free-energy functional given by

$$\mathscr{F} = \int_V \left\{ f(\rho, T) + \frac{\varepsilon^2}{2} |\nabla \rho|^2 \right\} dV \tag{13}$$

where V is a control volume, $f(\rho, T)$ is the bulk free-energy density (per unit volume), ε is a gradient energy coefficient, and T is the temperature. In a simple model $f(\rho, T)$ has a double-well form with respect to ρ beneath the critical temperature, T_C. The equilibrium situation may be considered by minimising $\mathscr{F}$ subject to the constraint of constant mass. In which case the Euler–Lagrange equation is given by

$$\varepsilon^2 \nabla^2 \rho - \frac{\partial f}{\partial \rho} + \lambda = 0 \tag{14}$$

where λ is the Lagrange multiplier associated with conservation of mass. This equation admits a one dimensional solution in which the density varies smoothly between two constant values. This solution represents a diffuse interface separating the different bulk densities associated with the liquid and gas phases. The interface region increases in width as the temperature increases towards the critical temperature because the double-well structure of $f(\rho, T)$ is lost in favour of a single well as $T \to T_C^-$.

3.1.2. Spinodal Decomposition of a Binary Alloy. Cahn and Hilliard$^{(8, 9)}$ developed a diffuse interface theory for spinodal decomposition in a binary alloy. In this situation they postulated a free-energy of the form

$$\mathscr{F} = \int_V \left\{ \frac{\varepsilon^2}{2} |\nabla c|^2 + f(c, T) \right\} dV \tag{15}$$

where V is the volume of the system, c denotes concentration, ε is the gradient energy coefficient and $f(c, T)$ represents the bulk free-energy density. Below the spinodal temperature, T_S, the bulk free-energy density, $f(c, T)$, has a double-well form with respect to c. The evolution equation for c is chosen consistent with the requirement that the free-energy of the system decays monotonically in time and that the total quantity of either component of the alloy is conserved:

$$\frac{\partial c}{\partial t} = -M \nabla \cdot \left\{ \nabla \frac{\delta \mathscr{F}}{\delta c} \right\} = M \nabla^2 \left\{ \varepsilon^2 \nabla^2 c - \frac{\partial f}{\partial c} \right\} \tag{16}$$

where M is a positive constant. For $T < T_S$ the Cahn–Hilliard equation supports interfaces of a width proportional to ε through which the concentration varies continuously between its bulk values given by the common tangent construction on the free energy curve $f(c, T)$.

3.1.3. Anti-phase Boundaries. Allen and Cahn$^{(10, 11)}$ studied anti-phase boundaries in a body centred cubic alloy. They are interfaces between regions ordered in the same manner but distinguished by a spatial translation. Here a single order parameter, ϕ, characterises the ordering of the bcc lattice, and Allen and Cahn employed a free energy of the system of the form

$$\mathscr{F} = \int_V \left\{ \frac{\varepsilon^2}{2} |\nabla\phi|^2 + g(\phi) \right\} dV \tag{17}$$

where $g(\phi)$ is a symmetric double-well of its argument. In this situation ϕ is not a conserved quantity (like the composition in the spinodal decomposition) and the requirement that the free-energy decreases monotonically in time is met by applying the dynamics:

$$\frac{\partial\phi}{\partial t} = -M \frac{\delta\mathscr{F}}{\delta\phi} = M \left[\varepsilon^2 \nabla^2\phi - \frac{\partial f}{\partial\phi} \right] \tag{18}$$

where $M > 0$.

3.1.4. Phase-Field Models of a Solid-Liquid Interface. More recently, Langer,$^{(18, 19)}$ developed a diffuse interface model of the first order phase transition between the solid and liquid of a pure material, commonly known as a phase-field model. In this formulation a function, $\phi(\vec{x}, t)$, is postulated whose value identifies the phase of the system, e.g., $\phi = 0$ solid and $\phi = 1$ liquid. It may be considered as playing the analogous role of the order parameter in the Cahn–Allen theory of anti-phase boundaries. However, in the setting of a first order phase transition between a solid and its liquid its physical interpretation is less clear. A Landau–Ginzburg free energy for the system is adopted of the form

$$\mathscr{F} = \int_V \left\{ \frac{\varepsilon^2}{2} |\nabla\phi|^2 + f(\phi, T) \right\} dV \tag{19}$$

where $f(\phi, T)$ is the bulk free energy of the system which has the form

$$f(\phi, T) = g(\phi) - L \frac{(T - T_M)}{T_M} p(\phi) \tag{20}$$

where $p(\phi)$ is a monotonic increasing function such that $p(0)=0$, and $p(1)=1$, L is the latent heat per unit volume, T_M is the melting temperature of the solid and again $g(\phi)$ is a symmetric double-well function of its argument. The equation for the phase field is motivated by requiring the free energy of the system decreases monotonically in time. It is given by

$$\frac{\partial \phi}{\partial t} = -M \frac{\delta \mathscr{F}}{\delta \phi} = M \left[\varepsilon^2 \nabla^2 \phi - \frac{\partial f(\phi, T)}{\partial \phi} \right] \tag{21}$$

The associated energy equation is given by

$$\rho c \frac{\partial T}{\partial t} = k \nabla^2 T - L \frac{\partial \phi}{\partial t} \tag{22}$$

where c is the heat capacity (per unit mass), and k is the thermal conductivity. Equation (21) and Eq. (22) are the so-called phase-field equations. Although their derivation briefly described above is ad hoc it can, as shown by Penrose and Fife,(20) Umantsev(21) Wang *et al.*,(22) Fife and Penrose(23) and Charach and Fife(24) be placed on a firmer physical footing in the framework of irreversible thermodynamics.(25)

3.1.5. Discussion. Above we have briefly described diffuse interface models of four different physical situations which, nevertheless, have several important features in common: A scalar order parameter which distinguishes the bulk phases, an underlying free-energy functional involving two terms in its integrand; a square gradient of the order parameter and bulk free energy with a double-well structure. In addition, the governing equation for the order parameter is chosen consistent with the second law of thermodynamics expressed as the requirement that the appropriate free energy should decrease in time. The generic form of the governing equation for a non-conserved order parameter is

$$\frac{\partial \phi}{\partial t} = M \left[\varepsilon^2 \nabla^2 \phi - \frac{\partial f(\phi)}{\partial \phi} \right] \tag{23}$$

To illustrate the main ideas we will focus on the case of a non-conserved order parameter when $f(\phi)$ is the double-well $f(\phi) = g(\phi) = \phi^2(1-\phi)^2/4a + bp(\phi)$, where $a(>0)$ and b are constants, and $p(\phi)$ is a monotonic function such that $p(0)=0$, $p(1)=1$. This corresponds to the Allen–Cahn equation when $b=0$ and the phase-field equation when $b \neq 0$. In one dimension the steady form Eq. (23) is

$$\varepsilon^2 \frac{d^2\phi}{dx^2} - \frac{\partial f(\phi)}{\partial \phi} = 0 \tag{24}$$

which has a first integral

$$\frac{\varepsilon^2}{2}\left[\frac{d\phi}{dx}\right]^2 - f(\phi) = \text{constant} \tag{25}$$

and for $b=0$ an exact solution

$$\phi(x) = \phi_0(x) = \frac{1}{2}\left[1+\tanh\left(\frac{x}{l}\right)\right] \tag{26}$$

where $l=2\sqrt{2}\,\varepsilon\sqrt{a}$. It corresponds to a stationary planar interface in which ϕ varies smoothly between its bulk values over a distance characterised by l that represents the interface thickness and, we observe, is proportional to the gradient energy coefficient.

The associated surface energy, γ, is given by the excess free energy of the system

$$\gamma = \int_{-\infty}^{\infty}\left\{\frac{\varepsilon^2}{2}\left|\frac{d\phi_0}{dx}\right|^2 + g(\phi_0)\right\}dx \tag{27}$$

which on using Eq. (25) may be expressed in the either of the following two forms

$$\gamma = \int_{-\infty}^{\infty}\varepsilon^2\left|\frac{d\phi_0}{dx}\right|^2 dx \qquad \text{or} \qquad \gamma = \int_0^1 \sqrt{2f(\phi)}\,d\phi \tag{28}$$

Using the exact solution Eq. (26) the surface energy is given as

$$\gamma = \frac{1}{6\sqrt{2}}\frac{\varepsilon}{\sqrt{a}} \tag{29}$$

Within the interface region the energy density is increased above its bulk value of zero for two reasons; $0<\phi<1$ and so the double-well bulk energy term $f(\phi)>0$, and $|\nabla\phi|>0$ providing a non-zero contribution from the gradient energy. These separate effects are made plain in the two expressions for the surface energy given in Eq. (28).

For $b\neq 0$ and the choice $p(\phi)=\phi^2(3-2\phi)$, $f(\phi)$ still retains its double-well minima at $\phi=0$ and 1 and there is an exact travelling wave solution of Eq. (23) given by $\phi(x,t)=\phi_0(x-Vt)$, when the speed of propagation of the interface is given by

$$V = -6\sqrt{2}\,M\varepsilon b\sqrt{a} \tag{30}$$

We note that both the surface energy of a planar interface for $b=0$ and the speed of propagation of a moving interface for $b\neq 0$ are isotropic in that they are independent of the orientation of the interface. We now go on to investigate anisotropic diffuse interface models.

3.2. Anisotropic Diffuse Interface Models

For phase transitions involving a crystalline solid phase the symmetries associated with the atomic lattice may be expressed in observable physical quantities, such as the surface energy, being anisotropic.

3.2.1. Phase-Field Model. An early attempt to include anisotropy into a phase-field model was due to Caginalp and Fife$^{(26)}$ who considered the case of a Bravais atomic lattice. They suggested modifying the square gradient in the free-energy functional:

$$\mathscr{F}=\int_V \left\{\frac{\varepsilon^2}{2}\left[a_1(\phi_x)^2+a_2(\phi_y)^2\right]+f(\phi,T)\right\} dV \tag{31}$$

which results in a "stretched" laplacian operator in the phase-field equation. Subsequently, Kobayashi$^{(27)}$ motivated by the dependence of the surface energy on ε in the expression for the surface energy in the isotropic case, Eq. (29), proposed that it be a function of the orientation of the direction of $\nabla\phi$, e.g., in two dimensions $\varepsilon(\theta)$, where θ is the polar angle that describes the direction of $\nabla\phi$. In this formulation the resulting phase-field equation appears rather complicated. In two dimensions it is given by

$$\begin{aligned}\frac{\partial\phi}{\partial t}=M\Big\{&\varepsilon^2(\theta)\,\nabla^2\phi+\varepsilon(\theta)\,\varepsilon'(\theta)\,\nabla\theta\cdot\nabla\phi\\ &+\frac{1}{2}\left[\varepsilon(\theta)\,\varepsilon'(\theta)\right]'\left[\phi_x\theta_y-\phi_y\theta_x\right]-\frac{\partial f(\phi)}{\partial\phi}\Big\}\end{aligned} \tag{32}$$

Kobayashi identified the surface energy anisotropy associated with this formulation as an important feature in the numerical simulation of dendritic solidification using the phase-field equations.

Taylor$^{(28)}$ suggested a more general formulation of the phase-field equations that includes models of Caginalp and Fife and Kobayashi as special cases. Again the starting point is the free-energy function. Taylor proposed the form

$$\mathscr{F}=\int_V \left\{\frac{\varepsilon^2}{2}\left[\Gamma(\nabla\phi)\right]^2+f(\phi,T)\right\} dV \tag{33}$$

where $\Gamma(\vec{p})$ is a homogeneous degree one function of its argument. The phase-field equation is then given by

$$\frac{\partial\phi}{\partial t} = -M\frac{\delta\mathscr{F}}{\delta\phi} = M\left\{\varepsilon^2\nabla\cdot[\Gamma(\nabla\phi)\,\vec{\xi}(\nabla\phi)] - \frac{\partial f}{\partial\phi}\right\} \tag{34}$$

where the cartesian components of $\vec{\xi}(\nabla\phi)$ are given by

$$\xi^j(\vec{p}) = \frac{\partial\Gamma(\vec{p})}{\partial p_j}, \qquad j = 1,..., 3 \tag{35}$$

and by comparison with the definition of the ξ-vector, Eq. (11), for the sharp interface we see that $\vec{\xi}(\nabla\phi)$ provides the natural extension of the definition of the ξ-vector to phasefield models. In contrast to the sharp interface case $\vec{\xi}(\nabla\phi)$ is a vector field which is defined throughout the *whole* domain, both within and outside the interfacial region, rather than just on the surface of the interface which is the case in the original Cahn–Hoffman formulation for a sharp interface model. The orientational dependence of the surface energy of a stationary planar interface is proportional to $\Gamma(\vec{v})$ where $\vec{v} = \nabla\phi/|\nabla\phi|$. For the case $f(\phi) = \phi^2(1-\phi)^2/4a$ it is given explicitly by

$$\gamma(\vec{v}) = \frac{\Gamma(\vec{v})}{6\sqrt{2}}\frac{\varepsilon}{\sqrt{a}} \tag{36}$$

3.2.2. Vector Phase-Field Model.

A recent extension of phase-field models to describe more than two phases with anisotropic interfaces, such as crystal grains, is due to Diepers *et al.*$^{(29)}$ and Nestler and Wheeler.$^{(30)}$ In this formulation an ensemble of N phases is modeled by employing N phase-field functions, ϕ_j, $j = 1,..., N$, such that

$$\sum_{j=1}^{N}\phi_j = 1 \tag{37}$$

The phase-field function, ϕ_α, identifies the phase labelled α, which is characterised by $\phi_j = 0$, $j \neq \alpha$, and $\phi_\alpha = 1$. We will regard the phase-field functions as the components of a phase-field vector $\vec{\phi} = (\phi_1, \phi_2,..., \phi_N)$. A free energy for the system is postulated of the form

$$\mathscr{F} = \int_V \mathscr{L}(\vec{\phi}, \nabla\vec{\phi})\,dV \tag{38}$$

where, in an analogous way to the anisotropic phase-field model for a solid-liquid interface, the Lagrangian density, $\mathscr{L}(\vec{\phi}, \nabla\vec{\phi})$, is given by

$$\mathscr{L}(\vec{\phi}, \nabla\vec{\phi}) = \sum_{\beta=1}^{N} \sum_{\alpha<\beta} \{\tfrac{1}{2}\varepsilon^2[\Gamma_{\alpha\beta}(\vec{r}_{\alpha\beta})]^2 + g_{\alpha\beta}(\vec{\phi})\} + \sum_{\alpha=1}^{N} b_\alpha(T)\,\phi_\alpha + \lambda\left[\sum_{\alpha=1}^{N}\phi_\alpha - 1\right] \tag{39}$$

Here

$$\vec{r}_{\alpha\beta} = \phi_\alpha \nabla\phi_\beta - \phi_\beta\nabla\phi_\alpha \tag{40}$$

$\Gamma_{\alpha\beta}(\vec{r}_{\alpha\beta})$ is defined to be a homogeneous degree one function of its argument, $g_{\alpha\beta}(\vec{\phi}) = \phi_\alpha^2\phi_\beta^2/4a_{\alpha\beta}$, with $a_{\alpha\beta}(=a_{\beta\alpha}) > 0$, represents the double-well component of the free-energy density between the phases α and β, and $b_\alpha(T)\,\phi_\alpha$ is the bulk free-energy density of phase α. The constraint Eq. (37) has been invoked with the Lagrange multiplier λ.

The governing equations are given by the gradient flow

$$\frac{\partial\phi_\mu}{\partial t} = -M(\nabla\vec{\phi})\,\frac{\delta\mathscr{F}}{\delta\phi_\mu}, \qquad \text{for} \quad \mu = 1,..., N \tag{41}$$

where $M(\nabla\vec{\phi})$ (>0) represents an anisotropic mobility. Using the form for the Lagrangian density, $\mathscr{L}(\vec{\phi}, \nabla\vec{\phi})$, Eq. (39), the governing equations are given explicity as

$$\frac{1}{M(\nabla\vec{\phi})}\,\frac{\partial\theta_\mu}{\partial t} = \sum_{\alpha\neq\mu}^{N}\left[\varepsilon^2[\nabla\cdot(\gamma_{\alpha\mu}(\vec{r}_{\alpha\mu})\,\vec{\xi}_{\alpha\mu}\phi_\alpha) + \gamma_{\alpha\mu}(\vec{r}_{\alpha\mu})\,\vec{\xi}_{\alpha\mu}\cdot\nabla\phi_\alpha] - \frac{1}{4}\frac{\partial g_{\alpha\mu}}{\partial\phi_\mu}\right] - b_\mu(T) - \lambda \tag{42}$$

for $\mu = 1,..., N$. The Lagrange multiplier may be found, using the constraint Eq. (37), to be

$$\lambda = \sum_{\mu=1}^{N}\phi_\mu\left\{\sum_{\alpha\neq\mu}^{N}\left[\varepsilon^2[\nabla\cdot(\Gamma(\vec{r}_{\alpha\mu})\,\vec{\xi}_{\alpha\mu}\phi_\alpha) + \gamma_{\alpha\mu}(\vec{r}_{\alpha\mu})\,\vec{\xi}_{\alpha\mu}\cdot\nabla\phi_\alpha] - \frac{1}{4}\frac{\partial g_{\alpha\mu}}{\partial\phi_\mu}\right] - \frac{1}{M(\nabla\vec{\phi})}\,\frac{\partial\phi_\mu}{\partial t} - b_\mu(T)\right\} \tag{43}$$

Here, $\vec{\xi}_{\alpha\beta}$ represents the ξ-vector between the phases labelled α and β which, in the spirit of Wheeler and McFadden,(40) is given by

$$\vec{\xi}_{\alpha\beta}(\vec{r}_{\alpha\beta}) = \frac{\partial\Gamma_{\alpha\beta}(\vec{r}_{\alpha\beta})}{\partial\vec{r}_{\alpha\beta}} = \nabla_{\vec{r}_{\alpha\beta}}\gamma_{\alpha\beta}(\vec{r}_{\alpha\beta}) \tag{44}$$

For the special case, $N=2$, corresponding to just two phases present, $\phi_1+\phi_2=1$, this model reduces to the standard anisotropic phase-field equation, Eq. (34), for either ϕ_1 or ϕ_2. The corresponding associated generalised ξ-vector's are

$$\vec{\xi}_{12}=\nabla_{\nabla\phi_1}\Gamma_{12}(\nabla\phi_1); \qquad \vec{\xi}_{21}=\nabla_{\nabla\phi_2}\Gamma_{21}(\nabla\phi_2) \tag{45}$$

and the surface energy of a planar interface is given by

$$\gamma_{12}=\frac{1}{6\sqrt{2}}\frac{\varepsilon}{\sqrt{a_{12}}}\Gamma_{12}(\vec{v}_{12}) \qquad \text{or} \qquad \gamma_{21}=\frac{1}{6\sqrt{2}}\frac{\varepsilon}{\sqrt{a_{21}}}\Gamma_{21}(\vec{v}_{21}) \tag{46}$$

where $\vec{v}_{12}=\nabla\phi_1/|\nabla\phi_1|$ and $\vec{v}_{21}=\nabla\phi_1/|\nabla\phi_2|$. Because the surface energy of an interface is unaffected by exchanging the two phases we find that $\Gamma_{12}(\vec{p})=\Gamma_{12}(-\vec{p})$, and hence from Eq. (45) that $\vec{\xi}_{12}=-\vec{\xi}_{21}$.

For the general case, $N>2$, we observe that there are $N(N-1)$ ξ-vectors, $\vec{\xi}_{\alpha\beta}(\vec{r}_{\alpha\beta})$. The vectors $\vec{r}_{\alpha\beta}$ and $\vec{r}_{\beta\alpha}(=-\vec{r}_{\alpha\beta})$ are both associated with the interface between the phases labelled α and β, which has surface energy proportional to $\Gamma_{\alpha\beta}(v_{\alpha\beta})$, where $v_{\alpha\beta}=\nabla\phi_\alpha/|\nabla\phi_\alpha|$. This formulation represents a natural extension of the anisotropic phase-field model for two phases using the generalised ξ-vector formulation.

Phase-field models assume that the form of surface energy anisotropy is known *a priori*, through the specification of the functions $\Gamma_{\alpha\beta}(\vec{p})$, determined by, for example, experiments or symmetry arguments based on the crystallographic structure of the material. It is rather at odds with the notion that phase-field models attempt to provide a description of the interior structure of the interface. This, along with the uncertain physical character of the phase-field variables, is a rather unsatisfactory state of affairs. We now describe a diffuse interface model of solid state ordering transitions in a face centred cubic (fcc) material where both these difficulties are addressed.

3.2.3. Multiple-Order-Parameter Models. We focus upon ordering transitions in a fcc alloy, e.g., $Cu-Au$. This situation has been considered by Kikuchi and Cahn$^{(31, 32)}$ using a discrete model based on the cluster variation method, Lai$^{(33)}$ and Braun *et al.*$^{(12)}$ who developed diffuse interface models which we now describe. The fcc lattice is shown schematically in Fig. 3 and consists of four interpenetrating cubic sublattices denoted *I*, *II*, *III*, *IV*, which we assume are decorated by either *A* or *B* atoms of the alloy. The variables ρ_I, ρ_{II}, ρ_{III}, ρ_{IV} denote the fractions of atom *A* on the four corresponding sublattices and, as such, they represent

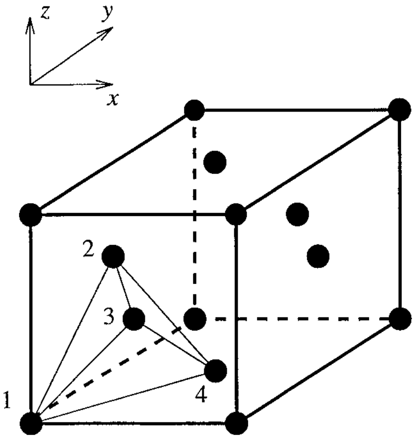

Fig. 3. A schematic of diagram of an fcc lattice showing the four sub-lattices labelled *I*, *II*, *III* and *IV*.

physically observable quantities. We define four corresponding order parameters by

$$X_0 = \tfrac{1}{4}[\rho_I + \rho_{II} + \rho_{III} + \rho_{IV}] \tag{47}$$

$$X_1 = \tfrac{1}{4}[\rho_I + \rho_{II} - \rho_{III} - \rho_{IV}] \tag{48}$$

$$X_2 = \tfrac{1}{4}[\rho_I - \rho_{II} + \rho_{III} - \rho_{IV}] \tag{49}$$

$$X_3 = \tfrac{1}{4}[\rho_I - \rho_{II} - \rho_{III} + \rho_{IV}] \tag{50}$$

Here, X_0, the average over the four sublattices represents the concentration of A, and X_1, X_2, X_3 are non-conserved order parameters that can vary between plus and minus one half and indicate the ordering on the lattice. Different uniform bulk phase are possible: A disordered phase in which there is no distinguished sublattice hence $\rho_I = \rho_{II} = \rho_{III} = \rho_{IV} = X_0$ and $X_1 = X_2 = X_3 = 0$; a $L1_2$ phase (using Strukturbericht notation) where one of the sublattices (I say) is distinguished from the others so $\rho_I \neq \rho_{II} = \rho_{III} = \rho_{IV}$ whence $X_1 = X_2 = X_3 \neq X_0$; a $L1_0$ phase in which two of the sublattices (I and II say) are distinguished from the remaining pair so $\rho_I = \rho_{II} \neq \rho_{III} = \rho_{IV}$ and hence $X_0 \neq X_1$ and $X_2 = X_3 = 0$. We limit our discussion to situations in which the composition is fixed.

The free energy for the system is assumed to have the form

$$\mathscr{F} = \int_V \left\{ \eta_{jlkm} \frac{\partial X_j}{\partial x_l} \frac{\partial X_k}{\partial x_m} + f(X_1, X_2, X_3) \right\} dV \tag{51}$$

where the term proportional to η_{jlkm} is the gradient energy contribution and $f(X_1, X_2, X_3)$ is the bulk energy term and we have employed the Einstein summation convention. Symmetry considerations that respect the underlying fcc lattice require that $f(X_1, X_2, X_3)$ is invariant to both cyclic permutations of its arguments and the interchange of the signs of any two of its arguments. Assuming a quartic polynomial form for $f(X_1, X_2, X_3)$ in the order parameters gives that

$$\begin{aligned} f(X_1, X_2, X_3) = {} & a_0 + a_2(X_1^2 + X_2^2 + X_3^2) + a_3 X_1 X_2 X_3 \\ & + a_{41}(X_1^4 + X_2^4 + X_3^4) + a_{42}(X_1^2 X_2^2 + X_2^2 X_3^2 + X_1^2 X_3^2) \end{aligned} \tag{52}$$

where a_2, a_{41}, a_{42} are assumed constant and a_0 is assumed to depend linearly on temperature. The bulk phases are given by local minima of the bulk free energy density.

Symmetry considerations also require that the gradient energy term has the form

$$\begin{aligned} & \frac{A}{2}\left[\left(\frac{\partial X_1}{\partial x}\right)^2 + \left(\frac{\partial X_2}{\partial y}\right)^2 + \left(\frac{\partial X_3}{\partial z}\right)^2\right] \\ & + \frac{B}{2}\left[\left(\frac{\partial X_1}{\partial y}\right)^2 + \left(\frac{\partial X_1}{\partial z}\right)^2 + \left(\frac{\partial X_2}{\partial x}\right)^2 + \left(\frac{\partial X_2}{\partial z}\right)^2 + \left(\frac{\partial X_3}{\partial x}\right)^2 + \left(\frac{\partial X_3}{\partial y}\right)^2\right] \end{aligned} \tag{53}$$

where A and B are constants. When $A = B$ this reduces to a square gradient form and represents the isotropic case. However, in general, the degree of anisotropy increases as $|1 - B/A|$ increases in value. The coefficients A and B may be interpreted as representing the bond energy of the nearest and second nearest neighbours on the lattice, see Braun *et al.*(12)

It is convenient to think of this model as a particular case of the class of diffuse interface models in which there are N non-conserved order parameters and the free energy of the system is given by

$$\mathcal{F} = \int_V \left\{\frac{\varepsilon^2}{2} \sum_{i=1}^{i=N} [\Gamma_i(\nabla X_i)]^2 + f(X_1, X_2, ..., X_N)\right\} dV \tag{54}$$

The governing equations for the order parameters are

$$\frac{\partial X_i}{\partial t} = -M \frac{\delta \mathcal{F}}{\delta X_i} \tag{55}$$

$$= M\left[\nabla \cdot (\Gamma_i(\nabla X_i)\, \vec{\xi}_i) - \frac{\partial f}{\partial X_i}\right] \tag{56}$$

for $i = 1,\ldots, N$. Here $\vec{\xi}_i$ are the so-called sub-ξ-vectors associated with each order parameter whose cartesian components are defined by

$$\vec{\xi}_i^{\,j} = \frac{\partial \Gamma_i(\nabla X_i)}{\partial X_{i,\,j}} \tag{57}$$

The fcc model is recovered for $N = 3$ when $\varepsilon = \sqrt{A}$ and

$$\Gamma_i(\nabla X_i) = \sqrt{a_{i1}\left(\frac{\partial X_i}{\partial x}\right)^2 + a_{i2}\left(\frac{\partial X_i}{\partial y}\right)^2 + a_{i3}\left(\frac{\partial X_i}{\partial z}\right)^2} \tag{58}$$

for $i = 1,\ldots, 3$, where

$$a_{ij} = B/A + (1 - B/A)\,\delta_{ij} \tag{59}$$

and δ_{ij} is the Kronecker delta.

In contrast to the previous phase-field models we are unable to immediately determine the surface energy of a planar interface (for $N > 1$), and in consequence make a direct connection with the ξ-vector of the corresponding sharp interface formulation. In the previous models the surface energy anisotropy was given explicity in terms of the homogeneous degree one functions occurring in the gradient energy terms, e.g., $\Gamma(\vec{n})$ in the scalar phase-field model. Here, the surface energy has to be determined from the model directly by computing the dependence of the excess free energy associated with a stationary planar interface with unit normal $\vec{n}$. In this one-dimensional situation the governing equations become:

$$[\Gamma_i(\vec{n})]^2 \frac{\partial^2 X_i}{\partial \rho^2} - \frac{\partial f}{\partial X_i} = 0 \tag{60}$$

subject to boundary conditions $X_i \to X_i^{\pm\infty}$ as $\rho \to \pm\infty$, where the coordinate ρ has been scaled so that $\varepsilon\rho$ measures distance through the interface, and $X_i^{\pm\infty}$ are the values of the order parameter in the bulk phases. The surface energy is given by

$$\gamma(\vec{n}) = \varepsilon \int_{-\infty}^{+\infty} \left\{ \tfrac{1}{2} \sum_{i=1}^{i=3} [\Gamma_i(\vec{n})]^2 \, [X_{i,\rho}]^2 + f - f^{\infty} \right\} d\rho \tag{61}$$

where f^{∞} is the free energy of the bulk phases. On using a first integral of Eq. (60) the surface energy may be expressed as

$$\gamma(\vec{n}) = \varepsilon \sum_{i=1}^{i=3} [\Gamma_i(\vec{n})]^2 \, \mathscr{I}_i(\vec{n}) \tag{62}$$

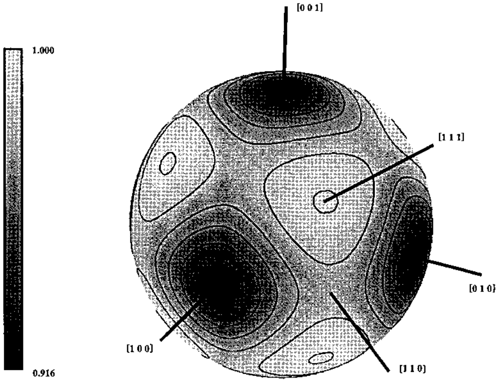

Fig. 4. The surface energy anisotropy computed from the multiple-order-parameter model (56).

where $\mathscr{I}_i(\vec{n})$ is the functional

$$\mathscr{I}_i(\vec{n})=\int_{-\infty}^{+\infty}[X_{i,\rho}]^2\,d\rho \tag{63}$$

Equation (62) represents the surface energy as a functional of the solution of Eq. (60). In Fig. 4 we show the dependence of the surface energy on the orientation of the interface, $\vec{n}$, calculated for the case of an interphase boundary for a fcc material between the disordered and $L1_2$ phases.

The general class of anisotropic models Eq. (54) and Eq. (55) contains, as a special case, the scalar anisotropic phase-field model discussed in Section 2.2.1 when $N=1$. When $N=3$ it also includes the diffuse interface model of phase transitions on a hexagonally closed packed lattice recently developed by Cahn, Han and McFadden.(34)

4. SHARP INTERFACE LIMIT

The relationship between diffuse interface and sharp interface models may be established by taking the, so-called, sharp interface limit. To illustrate the idea we initially focus our attention on the isotropic phase-field model discussed in Section 2.1.4. In that section we showed that the solution to the phase-field equation corresponding to a planar interface is $\phi_0(x-Vt)$, where the interface speed, V, is given by Eq. (30). Associated with this solution is an interface thickness, surface energy and a mobility given by

$$l=2\sqrt{2}\,\varepsilon\sqrt{a}, \qquad \gamma=\frac{1}{6\sqrt{2}}\frac{\varepsilon}{\sqrt{a}}, \qquad m=-6\sqrt{2}\,M\varepsilon b\sqrt{a} \tag{64}$$

respectively, where the mobility, m, is defined by $V = mb$ and $b = f(1) - f(0)$ is the bulk free energy difference. In general, we expect that the thickness of the interface will be small compared to its radius of curvature and in this situation the expressions given in Eq. (64) for a planar interface will remain good approximations when the interface is curved. With this in mind we non-dimensionalise using the following reference scales; length with respect to, R, a typical radius of curvature of the interface, time with respect to, τ, the thermal diffusion time, energy per unit volume with respect to γ/R. The non-dimensional forms of the interface thickness, surface energy and mobility are

$$\bar{l} = 2\sqrt{2}\,\bar{\delta}, \qquad \bar{\gamma} = 1 = \frac{1}{6\sqrt{2}}\frac{\bar{\delta}}{\bar{a}}, \qquad \bar{m} = 6\sqrt{2}\,\bar{M}\bar{\delta} \tag{65}$$

respectively, where

$$\bar{a} = \frac{a\gamma}{R}, \qquad \bar{\delta} = \frac{\varepsilon\sqrt{a}}{R}, \qquad \text{and} \quad \bar{M} = \frac{M\tau\varepsilon}{6\sqrt{2}\,R\sqrt{a}} \tag{66}$$

Here an overbar denotes a dimensionless quantity. We observe that the interface thickness is proportional to $\bar{\delta}$ and hence in the limit, $\bar{\delta} \to 0$, the interface thickness shrinks to zero; the sharp interface limit. In this limit Eq. (65) indicates that we require that $\bar{\delta} = 6\sqrt{2}\,\bar{a}$ and $\bar{M} = \bar{m}/(6\sqrt{2}\,\bar{\delta})$, where $\bar{m}$ is treated as an order one constant. The asymptotic analysis of the phase-field equation is conducted using a singular perturbation analysis. The solution is expanded in a regular perturbation series in the bulk phases (the "outer regions") away from the interface in a straightforward way. In the interface region (the "inner region") distance through the interface is resealed with respect to the dimensionless length scale, $\bar{\delta}$, characteristic of the dimensionless thickness of the interface. The solution is again expanded as a perturbation series in $\bar{\delta}$:

$$\phi = \phi^{(0)}(\rho) + \bar{\delta}\phi^{(1)}(\rho) + \mathcal{O}(\bar{\delta}^2) \tag{67}$$

Here $\rho = r/\bar{\delta}$, where (r, s) are body fitted coordinates; r and s locally represent dimensionless distance parallel to the normal and tangent directions to the curve $\phi = 1/2$ respectively. In dimensionless form the phase-field equation is

$$\frac{\partial\phi}{\partial\bar{t}} = \frac{\bar{m}}{\bar{\delta}^2}\left[\frac{d^2\phi}{d\rho^2} - \frac{d\bar{g}(\phi)}{d\phi} - \bar{\delta}\,\frac{\bar{b}}{6\sqrt{2}}\,\frac{dp(\phi)}{d\phi}\right] \tag{68}$$

Inserting the form for ϕ given by Eq. (67) into Eq. (68) gives at leading order that

$$\phi^{(0)}(\rho) = \frac{1}{2}\left[1 + \tanh\left(\frac{\rho}{2\sqrt{2}}\right)\right] \tag{69}$$

which is the dimensionless form of the solution Eq. (26) obtained above for a stationary planar interface. At next order the equation for $\phi^{(1)}(\rho)$ is given by

$$\frac{d^2\phi^{(1)}}{d\rho^2} - \phi^{(1)}\frac{d^2\bar{g}(\phi^{(0)})}{d\phi^2} = \frac{\bar{b}}{6\sqrt{2}}\frac{dp(\phi^{(0)})}{d\phi} - \left(\mathscr{K} + \frac{\bar{V}}{\bar{m}}\right)\frac{d\phi^{(0)}}{d\rho} \tag{70}$$

The linear operator on the left hand side is self adjoint and is satisfied by $d\phi^{(0)}/d\rho$, which gives the following solvability condition:

$$\left(\mathscr{K} + \frac{\bar{V}}{\bar{m}}\right)\int_{-\infty}^{+\infty}\left[\frac{d\phi^{(0)}}{d\rho}\right]^2 d\rho = \frac{\bar{b}}{6\sqrt{2}}\int_{-\infty}^{+\infty}\frac{dp(\phi^{(0)})}{d\phi}\frac{d\phi^{(0)}}{d\rho}\,d\rho \tag{71}$$

Evaluating the integrals and assuming that the free energy difference is $b = -L(T - T_M)/T_M$ where L is the latent heat per unit volume gives (in dimensional form)

$$T = T_M - \frac{\gamma T_M}{L}\mathscr{K} - \frac{1}{\mu}V \tag{72}$$

the Gibbs–Thomson equation modified for interface kinetics; μ is the so-called interface mobility which is related to the mobility m above by $\mu = Lm/T_M$.

The description of the sharp interface asymptotic analysis sketched above is for a particular distinguished limit which ensured that both kinetics and surface energy appeared as order one quantities in the Gibbs–Thomson equation. Caginalp(35) conducted the sharp interface analysis of the phase-field equations for a comprehensive range of distinguished limits and demonstrated that a range of free boundary problems were recovered. In addition, Karma(36) has found a new limit relevant to using phase-field models to compute dendritic growth a low undercoolings.

In the case of anisotropic surface energy the sharp interface asymptotic analysis has been conducted in a similar manner by refs. 37, 38, and 39 to recover the anisotropic Gibbs–Thomson equation which includes interface attachment kinetics. The more general three-dimensional case has been considered by Wheeler and McFadden(40) who exploited the ξ-vector formulation of the anisotropic phase-field model. The ξ-vector formulation has also been employed to good effect in conducting the sharp interface analysis in three dimensions for both the vector phase-field model[(30)] and the multiple order parameter model.[(41)] In the former case the sharp interface form of the ξ-vector is $\vec{\xi}_{\alpha\beta}(\vec{n})$ or $\vec{\xi}_{\beta\alpha}(\vec{n})$ at the interface between the phases labelled α and β. The latter case is more complicated. The sharp interface form of the ξ-vector is a linear combination of the sub-ξ-vectors given by

$$\vec{\xi} = \sum_{i=1}^{N} \vec{\xi}_i(\vec{n})\, \Gamma_i(\vec{n})\, \mathscr{I}_i(\vec{n}) \tag{73}$$

All these cases applied the same distinguished limit as described above and found that the resulting form to the Gibbs–Thomson equation included an anisotropic kinetic term, even when the mobilities in these equations (e.g., M in the phase-field equation) are assumed to be constant.

5. TYPE OF THE PHASE-FIELD EQUATION

In this section we show that the generalised ξ-vector plays an important role in determining the type of the phase-field equation This has been considered in two dimensions by Fife.[(42)] Courant and Hilbert[(43)] give the general theory of the type of partial differential equations.

To illustrate the ideas we restrict our discussion to the steady case. The anisotropic form of the steady phase-field equation is

$$\varepsilon^2 \nabla \cdot [\Gamma(\nabla\phi)\, \vec{\xi}(\nabla\phi)] - \frac{df(\phi)}{d\phi} = 0 \tag{74}$$

which is a quasi-linear partial differential equation that may be written as

$$\varepsilon^2 \sum_{j=1}^{j=3} \sum_{k=1}^{k=3} a_{jk} \frac{\partial^2 \phi}{\partial x_j x_k} - \frac{df(\phi)}{d\phi} = 0 \tag{75}$$

Here the coefficients a_{jk} are the components of the tensor

$$\mathbf{a} = \vec{\xi} \otimes \vec{\xi} + \Gamma(\nabla\phi)\, \nabla_{\vec{p}} \vec{\xi} \tag{76}$$

where $\vec{\xi}$ is regarded as a function of $\vec{p} = \nabla\phi$ and $\nabla_{\vec{p}}$ is the gradient operator with respect to the coordinates $\vec{p}$. In the two-dimensional case Eq. (75) expressed in cartesian coordinates is

$$\varepsilon^2 [a_{11}(\nabla\phi)\, \phi_{xx} + 2a_{12}(\nabla\phi)\, \phi_{xy} + a_{22}\phi_{yy}] - \frac{df(\phi)}{d\phi} = 0 \tag{77}$$

where

$$a_{11}(\nabla\phi)=\frac{1}{|\nabla\phi|^2}\{\Gamma(\theta)^2\,|\nabla\phi|^2-2\Gamma(\theta)\,\Gamma(\theta)'\,\phi_x\phi_y+[\Gamma(\theta)\,\Gamma(\theta)']'\,\phi_y^2\}$$

$$a_{12}(\nabla\phi)=\frac{1}{|\nabla\phi|^2}\{\Gamma(\theta)\,\Gamma(\theta)'\,[\phi_x^2-\phi_y^2]-[\Gamma(\theta)\,\Gamma(\theta)']'\,\phi_x\phi_y\}$$

$$a_{22}(\nabla\phi)=\frac{1}{|\nabla\phi|^2}\{\Gamma(\theta)^2\,|\nabla\phi|^2+2\Gamma(\theta)\,\Gamma(\theta)'\,\phi_x\phi_y+[\Gamma(\theta)\,\Gamma(\theta)']'\,\phi_x^2\}$$

Equation (77) may be recast as the first order system

$$\mathbf{C}\,\frac{\partial\vec{p}}{\partial x}+\mathbf{D}\,\frac{\partial\vec{p}}{\partial y}+\frac{1}{\varepsilon^2}\,\vec{g}=0$$

where

$$\mathbf{C}=\begin{pmatrix} a_{11} & 0 \\ 0 & -1 \end{pmatrix},\qquad \mathbf{D}=\begin{pmatrix} 2a_{12} & a_{22} \\ 1 & 0 \end{pmatrix},\qquad \vec{g}=\begin{pmatrix} -df/d\theta \\ 0 \end{pmatrix}$$

The characteristic equation is $|C-\tau D|=0$, which gives that

$$\tau=\frac{a_{12}(\nabla\phi)\pm i\,|\nabla\phi|^2\,\Gamma(\theta)^{3/2}\,\sqrt{\Gamma(\theta)+\Gamma(\theta)''}}{a_{22}(\nabla\phi)}$$

where $i=\sqrt{-1}$. Hence, the steady phase-field equation changes type when $\Gamma(\theta)+\Gamma(\theta)''$ changes sign; $\Gamma(\theta)+\Gamma(\theta)''>0$ it is elliptic, $\Gamma(\theta)+\Gamma(\theta)''=0$ parabolic, and $\Gamma(\theta)+\Gamma(\theta)''<0$ hyperbolic. In two dimensions the curvature of the $1/\gamma$-plot is proportional to $\gamma+\gamma''$ and hence to $\Gamma+\Gamma''$ (as γ is proportional to Γ). Thus the type of the steady phase-field equation at a point in space is determined by the sign of the curvature of the $1/\gamma$-plot in the direction parallel to $\nabla\phi$; if the $1/\gamma$-plot is convex then it is elliptic everywhere otherwise there may be regions of space where it is hyperbolic.

For $\Gamma+\Gamma''=0$, τ is a repeated root with value ξ^1/ξ^2, where ξ^1 and ξ^2 are the cartesian components of $\vec{\xi}$. Hence, there is a single family of characteristic curves everywhere parallel to the generalised ξ-vector. The corresponding characteristic equation is found to be

$$\varepsilon^2\vec{\xi}\cdot\frac{d\,\nabla\phi}{ds}=\frac{1}{\xi}\,\frac{df}{d\phi} \tag{78}$$

where $\xi = |\vec{\xi}|$, s denotes distance along the characteristic, and $\xi = |\vec{\xi}|$. Equation (78) can be written as

$$\varepsilon^2 \frac{d\Gamma(\nabla\phi)}{ds} - \frac{1}{\xi}\frac{df}{d\phi} = 0 \tag{79}$$

which may be integrated using the property of the ξ-vector that $d\Gamma = \vec{\xi} \cdot d\vec{p}$ to give that $\varepsilon^2 \Gamma(\nabla\phi)^2/2 - f(\phi)$ is constant along the characteristic. We note that this is the same conserved quantity that emerges in the one-dimensional form of the steady phase-field equation; the anisotropic form of Eq. (25).

The type of the steady phase-field equation may be studied for the three dimensional case using a different approach which examines the form of of the differential operator appearing in Eq. (74) in a new system of coordinates. In Appendix A we evaluate the components of the tensor **a** in a system of coordinates (s_1, s_2, s_3) which are locally body fitted to the $1/\Gamma$ surface and find that the local form of the differential operator of the phase-field equation is

$$\varepsilon^2 \left\{ \Gamma(\nabla\phi)\, \mathscr{K}_1 \left[\xi \frac{\partial^2\phi}{\partial(s^1)^2} - 2\alpha_1 \frac{\partial^2\phi}{\partial s^2\, \partial s^3} \right] + \Gamma(\nabla\phi)\, \mathscr{K}_2 \left[\xi \frac{\partial^2\phi}{\partial(s^2)^2} - 2\alpha_2 \frac{\partial^2\phi}{\partial s^2\, \partial s^3} \right] \right.$$
$$\left. + \left[\frac{\partial}{\partial s^3} \left(\Gamma(\vec{p}) \frac{\partial\gamma(\vec{p})}{\partial s^3} \right) \right] \frac{\partial^2\phi}{\partial(s^3)^2} \right\} \tag{80}$$

where α_1 and α_2 are constants and $\mathscr{K}_1$ and $\mathscr{K}_2$ are the principal curvatures on the $1/\Gamma$ surface. This shows that the phase-field equation will change type when either of the principal curvatures of the $1/\gamma$-plot changes sign, i.e., it looses its convexity (as in two dimensions).

6. THERMODYNAMIC BASIS OF PHASE-FIELD MODELS

In this section we review the thermodynamic basis of the phase-field model and show how the notion of a stress tensor emerges naturally from the underlying variational principal as well as from irreversible thermodynamics when motion of the material is allowed.

6.1. Thermodynamic Interpretation of $\vec{\xi}$

Our starting pointing point is the entropy for a material volume $\Omega(t)$ which we write as the gradient energy functional

$$\mathscr{S} = \int_{\Omega(t)} \left[\rho s - \tfrac{1}{2}\varepsilon_S^2 \Gamma^2(\nabla\phi) \right] dV \tag{81}$$

where ρ is the density and s is the entropy per unit mass. The first term in the integrand, ρs, is the classical entropy density (per unit volume) and the second is a nonclassical term associated with spatial gradients of the phase field. Here the gradient entropy coefficient ε_S is assumed to be a constant. The internal energy, $\mathscr{E}$, associated with the material volume is assumed to have the form

$$\mathscr{E} = \int_{\Omega(t)} \rho e \, dV \tag{82}$$

where e is the internal energy per unit mass. The internal energy balance law is

$$\frac{d\mathscr{E}}{dt} + \int_{\delta\Omega(t)} \vec{q}_E \cdot \vec{n} \, dA = 0 \tag{83}$$

where $\vec{n}$ is the outward unit normal to $\delta\Omega(t)$ and $\vec{q}_E$ is the internal energy flux. In addition, the entropy balance takes the form

$$\frac{d\mathscr{S}}{dt} + \int_{\delta\Omega(t)} \vec{q}_S \cdot \vec{n} \, dA = \int_{\Omega(t)} \dot{s}^{prod} \, dV \tag{84}$$

where $\vec{q}_S$ is the entropy flux and $\dot{s}^{prod}$ is the local rate of entropy production. The second law of thermodynamics is then expressed by the requirement that $\dot{s}^{prod}$ is positive.

To proceed we recast the conservation laws (83)–(84) as differential equations. These are used to express the local entropy production in terms of the fluxes $\vec{q}_E$, and $\vec{q}_S$, as well $\partial\phi/\partial t$ as

$$\begin{aligned} \dot{s}^{prod} = {} & \frac{1}{T} \left\{ \varepsilon_F^2 \nabla \cdot (\Gamma(\nabla\phi)\, \vec{\xi}\,) - \rho \frac{\partial e}{\partial \phi} \right\} \frac{\partial \phi}{\partial t} \\ & + \nabla \cdot \left(\vec{q}_S - \frac{\vec{q}_E}{T} - \frac{\varepsilon_F^2}{T} \Gamma(\nabla\phi)\, \vec{\xi}\, \frac{\partial \phi}{\partial t} \right) + \vec{q}_E \cdot \nabla \left(\frac{1}{T} \right) \end{aligned} \tag{85}$$

where $\varepsilon_F^2 = T\varepsilon_S^2$. We may ensure that $\dot{s}^{prod}$ is positive by putting

$$\frac{\partial \phi}{\partial t} = M \left\{ \varepsilon_F^2 \nabla \cdot (\Gamma(\nabla\phi)\, \vec{\xi}\,) - \rho \frac{\partial e}{\partial \phi} \right\} \tag{86}$$

and

$$\vec{q}_E = \tilde{k}\, \nabla \left(\frac{1}{T} \right) - \varepsilon_E^2 \Gamma(\nabla\phi)\, \vec{\xi}\, \frac{\partial \phi}{\partial t}, \qquad \vec{q}_S = \frac{\tilde{k}}{T} \nabla \left(\frac{1}{T} \right) + \varepsilon_S^2 \Gamma(\nabla\phi)\, \vec{\xi}\, \frac{\partial \phi}{\partial t} \tag{87}$$

where $\tilde{k}/T^2$ is the thermal conductivity. We observe for the case when the density is constant that the phase-field equation, Equation (34), is consistent with the second law of thermodynamics. Further, we note that the part of the internal energy and entropy fluxes due to the change of state, rather than heat flow, is in the direction parallel to the ξ-vector.

6.2. Stress Tensor

The procedure briefly described above to obtain the entropy production can be extended to allow for motion of matter. In this case the kinetic energy must be included in the total energy $\mathscr{E}$ by the addition of a term $\rho u^2/2$ in the integrand of Eq. (82) where $\vec{u}$ is the velocity of the material. An additional balance law is asserted for linear momentum. Further details can be found in Anderson *et al.*(44, 45) who have recently included convection into a phase-field model of a pure material using this approach. In the isothermal case the form for the entropy production is then

$$\dot{s}^{prod} = \frac{1}{T}\left\{\mathbf{m} + \varepsilon_F^2 \Gamma(\nabla\phi)\,\vec{\xi}\otimes\nabla\phi + \left[p - \frac{\varepsilon_F^2}{2}\Gamma(\nabla\phi)^2\right]\mathbf{I}\right\} : \nabla\vec{u}$$
$$+\frac{1}{T}\left\{\varepsilon_F^2\,\nabla\cdot(\Gamma(\nabla\phi)\,\vec{\xi}) - \rho\frac{\partial e}{\partial\phi}\right\}\frac{D\phi}{Dt} + \nabla\cdot\left(\vec{q}_s - \frac{\vec{q}_E}{T} - \frac{\varepsilon_F^2}{T}\Gamma(\nabla\phi)\,\vec{\xi}\,\frac{D\phi}{DT}\right) \tag{88}$$

where $\mathbf{m}$ is the stress tensor, p is the pressure, and $D/Dt \equiv \partial/\partial t + \vec{u}\cdot\nabla$ is the material derivative. The first term is new and arises due to the motion of the matter. We observe that the stress tensor has a part,

$$\mathbf{\Xi} = \left[-p + \frac{\varepsilon_F^2}{2}\Gamma(\nabla\phi)^2\right]\mathbf{I} - \varepsilon_F^2\Gamma(\nabla\phi)\,\vec{\xi}\otimes\nabla\phi \tag{89}$$

which does not contribute to the entropy production; the so-called reversible part of the stress tensor. Fried and Gurtin(46, 47) and Gurtin(48) first identified this stress tensor by adopting an alternative mechanical approach.

The stress tensor also results directly from the variational formulation of the equilibrium situation, in which the energy of the system is minimised subject to the constraints of fixed total mass and entropy. We set

$$\delta\int_V\left[\rho e - \lambda_S\rho s - \lambda_M\rho + \frac{\lambda_S\varepsilon_S^2}{2}\Gamma^2(\nabla\phi)\right]dV = 0 \tag{90}$$

where λ_S and λ_M are Lagrange multipliers associated with the constraints on entropy and mass respectively. Taking variations with respect to δs, $\delta\rho$, and $\delta\phi$ gives $\lambda_S = T$ and $\lambda_M = \mu$, the chemical potential. It follows that $\lambda_S \varepsilon_S^2 = \varepsilon_F^2$. At equilibrium, the integrand in Eq. (90) can therefore be expressed in the form $\mathscr{L} = -p + \frac{1}{2}\varepsilon_F^2 \Gamma^2(\nabla\phi)$. We observe that $\mathscr{L}$ is translationally invariant and hence Noether's theorem[(49)] shows that there exists a divergence free tensor

$$\mathscr{L}\mathbf{I} - \frac{\partial \mathscr{L}}{\partial \nabla\phi} \otimes \nabla\phi = \left(-p + \frac{\varepsilon_F^2}{2} \Gamma(\nabla\phi)^2 \right) \mathbf{I} - \varepsilon_F^2 \Gamma(\nabla\phi)\, \vec{\xi} \otimes \nabla\phi \qquad (91)$$

which we note is identical to the Ξ-tensor.

In general the Ξ tensor is not symmetric and there is an associated body couple distribution $\varepsilon^2 \Gamma(\nabla\phi)\, \nabla\phi \times \vec{\xi}$. Hence surface energy anisotropy induces a body couple within the interface. This is because anisotropy allows the interface to reduce its surface energy by local rotation as well as curve shortening which is the only mechanism available when the surface energy is isotropic. Wheeler and McFadden[(41)] show that in the sharp interface limit the force per unit length acting on a line element within the interface is identical to Eq. (8) obtained by Hoffman and Cahn.[(1)]

The Ξ tensor has numerous other uses: When allied to the divergence theorem it provides a succinct derivation of the anisotropic form of the Gibbs Thomson equation (7) in the sharp interface limit using a pill-box control volume,[(50)] as well as force balances for edges and multijunctions. It is the latter two applications that we now consider.

6.2.1. Edges. When the surface energy is so pronounced that the $1/\gamma$-plot is not convex then, as we have seen above, the steady phase-field equations are hyperbolic and the Wulff equilibrium shape will include missing orientations, e.g., edges. We therefore anticipate that solutions of the phase-field equation will allow solutions that involve shocks to represent the edges. Wheeler and McFadden[(41)] showed that in this situation the edge comprised the junction of two diffuse interfaces at which ϕ is continuous but $\nabla\phi$ is not. The situation is sketched in Fig. 5 in which two interfaces, labelled 1 and 2 intersect to form an edge. We construct a cylindrical control surface, S, which contains the the edge region and perpendicularly intersects the two interfaces far away from the edge; the contributions from the end caps of the cylinder can be ignored. The divergence theorem gives

$$\int_S \mathbf{\Xi} \cdot \vec{n}\, dA = 0 \qquad (92)$$

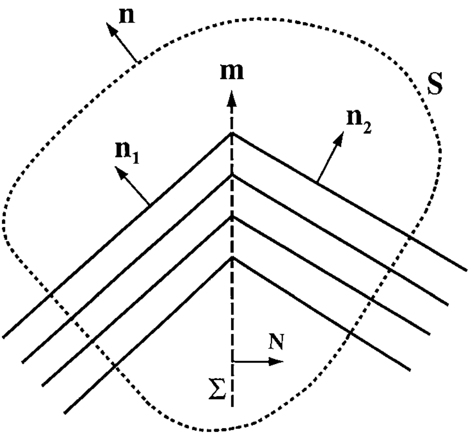

Fig. 5. A schematic diagram of an edge. The control surface S cuts the diffuse interfaces at right angles. The vector $\vec{l}$, in the direction of $\vec{n}_1 \times \vec{n}_2$, points into the page. The vector $\vec{N}$ is the unit normal to the surface of discontinuity, Σ.

where $\vec{n}$ is the unit normal to S. In the, bulk regions away from the interfaces Ξ is zero and so the only the non-zero contributions are from the parts of S which intersect the interfaces. If we now take the sharp interface limit then we find that

$$\vec{\xi}_1 \times \vec{l} + \vec{\xi}_2 \times \vec{l} = 0 \tag{93}$$

where $\vec{\xi}_1$ and $\vec{\xi}_2$ are the ξ-vectors associated with each interface evaluated at the edge. This is the same equation as given by Cahn and Hoffman; it represents a force balance for the edge in the plane normal to $\vec{l}$ and requires that the component of the ξ-vector perpendicular to the edge direction $\vec{l}$ is continuous.

The jump conditions on the phase field at the surface Σ on which $\nabla\phi$ is discontinuous may be examined by minimising the underlying free energy subject to the constraint that ϕ is continuous on Σ. This results in the conditions

$$\Gamma_1 \vec{\xi}_1 \cdot \vec{N} = \Gamma_2 \vec{\xi}_2 \cdot \vec{N} = \left[\frac{1}{2}(\Gamma_1^2 - \Gamma_2^2)\right] \Big/ \left[\frac{\partial \phi_1}{\partial N} - \frac{\partial \phi_2}{\partial N}\right] \tag{94}$$

at Σ. It resembles a common tangent condition. For the special case of two flat interfaces it recovers (93) and gives that the tangent vector to Σ, denoted $\vec{m}$ in Fig. 5, is parallel to

$$\vec{\xi}_1 - [\vec{\xi}_1 \cdot \vec{l}]\,\vec{l} = \vec{\xi}_2 - [\vec{\xi}_2 \cdot \vec{l}]\,\vec{l} \tag{95}$$

i.e., the plane Σ is spanned by $\vec{l}$ and the common component of the two ξ-vectors which is orthogonal to $\vec{l}$.

6.2.2. Multi-junctions. The vector phase-field model and the multiple-order-parameter model both allow for the existence of more than two bulk states and hence the possibility of multiple junctions where several bulk states meet. A divergence-free stress tensor may be derived, using Noether's theorem, for these models as well. It is given by

$$\Xi_V = \varepsilon^2 \sum_{\beta=1}^{N} \sum_{\alpha<\beta} \Gamma_{\alpha\beta}(\vec{r}_{\alpha\beta})\, \vec{\xi}_{\alpha\beta} \otimes \vec{r}_{\alpha\beta} + \mathscr{L}(\vec{\phi}, \nabla\vec{\phi})\, \mathbf{I} \tag{96}$$

for the vector phase-field model where $\mathscr{L}(\vec{\phi}, \nabla\vec{\phi})$ is the Lagrangian density given by Eq. (39), and

$$\Xi_M = \varepsilon^2 \sum_{i=1}^{N} \Gamma_i(\nabla X_i)\, \vec{\xi}_i \otimes \nabla X_i + \left\{ \frac{\varepsilon^2}{2} \sum_{i=1}^{N} \Gamma_i(\nabla X_i)^2 + f \right\} \mathbf{I} \tag{97}$$

for the multiple-order-parameter model. To examine a stationary multi-junction we again construct a control surface, S, which contains the junction and perpendicularly intersects the interfaces emanating from it. Applying the divergence theorem and evaluating the non-zero parts of the surface integral from the interfacial regions in the sharp interface limit gives

$$\vec{l} \times \sum_{i=1}^{i=N} \vec{\xi}_i = 0 \tag{98}$$

where $\vec{l}$ is the unit vector parallel to the junction. This again is the same result given by Hoffman and Cahn. It represents a force balance at the junction; for the isotropic case it reduces to Young's Law.

6.2.3. Conserved Order Parameter Models. The stress tensor may also be derived for conserved order parameter models using Noether's Theorem applied to the equilibrium situation. The conserved quantity is invoked with the introduction of a Lagrange multiplier. For the Cahn–Hilliard equation it is given by

$$\Xi_{CH} = -\varepsilon^2\, \nabla c \otimes \nabla c + \{ \varepsilon^2 [c\, \nabla^2 c + \tfrac{1}{2} |\nabla c|^2] + f(c) - c f_c \}\, \mathbf{I} \tag{99}$$

and for the case of a critical fluid it is given by

$$\Xi_{CF} = -\varepsilon^2\, \nabla\rho \otimes \nabla\rho + \varepsilon^2 (\rho\, \nabla^2 \rho + \tfrac{1}{2} |\nabla\rho|^2)\, \mathbf{I} \tag{100}$$

This is the so-called capillary tensor first identified by Korteweg.(51)

7. KINETICS

The concept of a ξ-vector also plays a useful role in front propagation in anisotropic media where the front speed depends on its orientation:

$$v_n = \mu(\vec{n}) \tag{101}$$

Here $\vec{n}$ is the outward unit normal to the front. This is a situation that arises in many areas from wave propagation in an æolotropic linearly elastic medium (see Musgrave$^{(52)}$) to the kinetically controlled growth of a crystal into an undercooked melt.

We define the cartesian components of the ξ-vector in the same way as before

$$\xi^j = \frac{\partial \mu(\vec{p})}{\partial p^j} \tag{102}$$

where $\mu(\vec{p})$ is the homogeneous degree one extension of $\mu(\vec{n})$. We put $\vec{r} = t\vec{\xi}$ and note that

$$v_n = \frac{d\vec{r}}{dt} \cdot \vec{n} = \vec{\xi} \cdot \vec{n} = \mu(\vec{n}) \tag{103}$$

where the last step follows from the property of the ξ-vector given by Eq. (5). Hence we find that $\vec{r} = t\vec{\xi}$ provides an exact solution to Eq. (101). The ξ-plot provides the self-similar shape of the front that is achieved at long times. In the setting of anisotropic elastic waves the $1/\mu$-plot is the slowness surface which plays a prominent role in their theoretical description. In the context of kinetically controlled crystal growth Frank$^{(53)}$ showed that a Gibbs–Wulff construction based on the $\mu(\vec{n})$-plot could be used to determine the long-time growth shape, which in view of the equivalence of the ξ-plot and the Gibbs–Wulff construction is consistent with the solution $\vec{r} = t\vec{\xi}$.

Braun *et al.*$^{(54)}$ have recently combined the diffuse interface and sharp interface approaches. They employed the multiple-order-parameter model of ordering transitions in an fcc material discussed in Section 3.2.3 to determine numerically the mobility function $\mu(\vec{n})$ for some particular antiphase boundaries. They used this to determine the resulting long-time interface shapes for kinetically controlled growth by computing the ξ-vector of the corresponding sharp interface model, and in particular to study the effect increasing the degree of anisotropy characterized by the ratio of the gradient energy coefficients B/A in Eq. (59).

8. CONCLUSION

In this paper we have reviewed two important theoretical developments to which J. W. Cahn has made major contributions: The theory of the ξ-vector developed by Hoffman and Cahn that provides an elegant setting for the analysis of the equilibrium shapes of sharp interfaces in the presence of anisotropic surface energy, and diffuse interface theories of interfaces with anisotropic surface energy. We have described recent work which connects these two aspects by the development of a generalized ξ-vector for diffuse interface models. We have shown that the ξ-vector plays a central role in the diffuse interface theory: It provides a useful means of examining the sharp interface limit; it is related to the entropy flux associated with the interface motion; it forms an essential part of the reversible part of the associated stress tensor whereby it allows a connection to the notion of stress in the interface.

APPENDIX A. 1/Γ-FITTED COORDINATES

We consider $\mathbf{a} = \vec{\xi} \otimes \vec{\xi} + \Gamma(\nabla\phi)\, \nabla_{\vec{p}}\vec{\xi}$ in the vicinity of some point $\vec{p}_0$. We introduce surface fitted coordinates to the $1/\Gamma$ surface, denoted $\mathscr{P}_0$, defined by $|\vec{p}| = A/\Gamma(\vec{p}/|\vec{p}|)$ where A is a constant, which passes through $\vec{p}_0$. To this end we define new coordinates (s^1, s^2, s^3) by

$$\vec{p} = \vec{P}(s^1, s^2) + s^3\vec{n}(s^1, s^2) \tag{104}$$

where $\vec{p} = \vec{P}(s^1, s^2)$ is the surface $\mathscr{P}_0$, $\vec{n}(s^1, s^2)$ is the normal to $\mathscr{P}_0$ and s^1 and s^2 parameterise $\mathscr{P}_0$ and measure distance in the direction of the principal directions at $\vec{p}_0$. The basis vectors are

$$\begin{aligned} \vec{e}_1 &= [1 + s^3\mathscr{K}_1(s^1, s^2)]\; \vec{t}_1(s^1, s^2) \\ \vec{e}_2 &= [1 + s^3\mathscr{K}_2(s^1, s^2)]\; \vec{t}_2(s^1, s^2) \\ \vec{e}_3 &= \vec{n} \end{aligned} \tag{105}$$

where $\vec{t}_1(s^1, s^2)$ and $\vec{t}_2(s^1, s^2)$ are orthonormal tangent vectors to $\mathscr{P}_0$ and $\mathscr{K}_1$, $\mathscr{K}_2$ are its principal curvatures. The metric tensor is

$$g_{ij} = \begin{pmatrix} [1 + s^3\mathscr{K}_1(s^1, s^2)]^2 & 0 & 0 \\ 0 & [1 + s^3\mathscr{K}_2(s^1, s^2)]^2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{106}$$

We now evaluate $\vec{\xi}$ in this coordinate system. The ξ-vector is defined by $\nabla\Gamma(\vec{p})$ and is given by

$$\begin{aligned}\vec{\xi} &= \frac{\partial\Gamma(\vec{p})}{\partial s^1}\,\tilde{\omega}^1 + \frac{\partial\Gamma(\vec{p})}{\partial s^2}\,\tilde{\omega}^2 + \frac{\partial\Gamma(\vec{p})}{\partial s^3}\,\tilde{\omega}^3 \\ &= \frac{1}{[1+s^3\mathscr{K}_1(s^1,s^2)]^2}\frac{\partial\Gamma(\vec{p})}{\partial s^1}\,\vec{t}_1 + \frac{1}{[1+s^3\mathscr{K}_2(s^1,s^2)]^2}\frac{\partial\Gamma(\vec{p})}{\partial s^2}\,\vec{t}_2 + \frac{\partial\Gamma(\vec{p})}{\partial s^3}\,\vec{n}\end{aligned} \tag{107}$$

where the $\tilde{\omega}^1$, $\tilde{\omega}^2$, $\tilde{\omega}^3$ are the reciprocal basis vectors.

Now $\vec{\xi}$ is in the direction of the normal to the $1/\Gamma$-plot so $\vec{\xi}$ on the surface $\mathscr{P}_0$ is given by $|\vec{\xi}(s^1, s^2, 0)|\,\vec{n}$ and we deduce that

$$\left.\frac{\partial\Gamma(\vec{p})}{\partial s^1}\right|_{s^3=0} = \left.\frac{\partial\Gamma(\vec{p})}{\partial s^2}\right|_{s^3=0} = 0 \tag{108}$$

and

$$|\vec{\xi}(s^1, s^2, 0)| = \left.\frac{\partial\Gamma(\vec{p})}{\partial s^3}\right|_{s^3=0} \tag{109}$$

Moreover, $\vec{\xi}$ satisfies $\Gamma(\vec{p}) = \vec{\xi}\cdot\vec{p}$, and hence on $\mathscr{P}_0$

$$\Gamma(\vec{P}) = |\vec{\xi}(s^1, s^2, 0)|\,\vec{n}\cdot\vec{P}(s^1, s^2) \tag{110}$$

and so

$$|\vec{\xi}(s^1, s^2, 0)| = \frac{\Gamma(\vec{P})}{\vec{n}\cdot\vec{P}(s^1, s^2)} \tag{111}$$

Thus

$$\frac{\partial\,|\vec{\xi}(s^1, s^2, 0)|}{\partial s^1} = \frac{1}{\vec{n}\cdot\vec{P}(s^1, s^2)}\left.\frac{\partial\Gamma(\vec{P})}{\partial s^1}\right|_{s^3=0} - \frac{\Gamma(\vec{P})}{[\vec{n}\cdot\vec{P}(s^1, s^2)]^2}\left[\vec{P}\cdot\frac{\partial\vec{n}}{\partial s^1} + \vec{n}\cdot\frac{\partial\vec{P}}{\partial s^1}\right] \tag{112}$$

which simplifies to give

$$\frac{\partial\,|\vec{\xi}(s^1, s^2, 0)|}{\partial s^1} = -\alpha_1\mathscr{K}_1 \tag{113}$$

where

$$\alpha_1 = \frac{\Gamma(\vec{P})\,\vec{t}_1(s^1, s^2)\cdot\vec{P}(s^1, s^2)}{[\vec{n}\cdot\vec{P}(s^1, s^2)]^2} \tag{114}$$

Similarly

$$\frac{\partial\,|\vec{\xi}(s^1, s^2, 0)|}{\partial s^2} = -\alpha_2 \mathscr{K}_2 \tag{115}$$

where

$$\alpha_2 = \frac{\Gamma(\vec{P})\ \vec{t}_2(s^1, s^2) \cdot \vec{P}(s^1, s^2)}{[\vec{n} \cdot \vec{P}(s^1, s^2)]^2} \tag{116}$$

Using these results we find that

$$\frac{\partial\vec{\xi}(s^1, s^2, 0)}{\partial s^1} = \frac{\partial\,|\vec{\xi}(s^1, s^2, 0)|}{\partial s^1}\,\vec{n} + |\vec{\xi}(s^1, s^2, 0)|\,\frac{\partial\vec{n}}{\partial s^1} = [\,|\vec{\xi}(s^1, s^2, 0)|\ \vec{t}_1 - \alpha_1\vec{n}]\ \mathscr{K}_1 \tag{117}$$

and similarly

$$\frac{\partial\vec{\xi}(s^1, s^2, 0)}{\partial s^2} = [\,|\vec{\xi}(s^1, s^2, 0)|\ \vec{t}_2 - \alpha_2\vec{n}]\ \mathscr{K}_2 \tag{118}$$

Now

$$\begin{aligned}\frac{\partial\vec{\xi}(s^1, s^2, s^3)}{\partial s^3} &\\ = \Bigg[&\frac{1}{[1 + s^3\mathscr{K}_1(s^1, s^2)]^2}\,\frac{\partial^2\Gamma(\vec{p})}{\partial s^3 s^1} - 2\,\frac{\mathscr{K}_1(s^1, s^2)}{[1 + s^3\mathscr{K}_1(s^1, s^2)]^3}\,\frac{\partial\Gamma(\vec{p})}{\partial s^1}\Bigg]\ \vec{t}_1\\ &+ \Bigg[\frac{1}{[1 + s^3\mathscr{K}_2(s^1, s^2)]^2}\,\frac{\partial^2\Gamma(\vec{p})}{\partial s^3 s^2} - 2\,\frac{\mathscr{K}_2(s^1, s^2)}{[1 + s^3\mathscr{K}_2(s^1, s^2)]^3}\,\frac{\partial\Gamma(\vec{p})}{\partial s^1}\Bigg]\ \vec{t}_2\\ &+ \frac{\partial^2\Gamma(\vec{p})}{\partial(s^3)^2}\,\vec{n}\end{aligned}$$

Also

$$\frac{\partial^2\Gamma(\vec{p})}{\partial s^3 s^1} = \frac{\partial}{\partial s^1}\left(\frac{\partial\Gamma(\vec{p})}{\partial s^3}\right) = \frac{\partial\,|\vec{\xi}|}{\partial s^1} = -\alpha_1\mathscr{K}_1 \tag{119}$$

and so

$$\left.\frac{\partial\vec{\xi}(s^1, s^2, s^3)}{\partial s^3}\right|_{s^3=0} = -\alpha_1\mathscr{K}_1(s^1, s^2)\ \vec{t}_1 - \alpha_2\mathscr{K}_2(s^1, s^2)\ \vec{t}_2 + \left.\frac{\partial^2\Gamma(\vec{p})}{\partial(s^3)^2}\right|_{s^3=0}\vec{n} \tag{120}$$

Hence, expressed in matrix form in this coordinate system, the components of $\nabla\vec{\xi}|_{s^3=0}$ are

$$(\nabla\vec{\xi}|_{s^3=0})^i_j=\begin{pmatrix} |\vec{\xi}(s^1,s^2,0)|\,\mathscr{K}_1 & 0 & -\alpha_1\mathscr{K}_1 \\ 0 & |\vec{\xi}(s^1,s^2,0)|\,\mathscr{K}_2 & -\alpha_2\mathscr{K}_2 \\ -\alpha_1\mathscr{K}_1 & -\alpha_2\mathscr{K}_2(s^1,s^2) & \left.\dfrac{\partial^2\Gamma(\vec{p})}{\partial(s^3)^2}\right|_{s^3=0} \end{pmatrix} \tag{121}$$

Also in this coordinate system $\vec{\xi}\otimes\vec{\xi}$ expressed in matrix form is

$$(\vec{\xi}(s^1,s^2,0)\otimes\vec{\xi}(s^1,s^2,0))^i_j=\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & |\vec{\xi}|^2 \end{pmatrix} \tag{122}$$

Hence, at $\vec{p}_0$, **a** in this coordinate system has the form

$$(\vec{\xi}\otimes\vec{\xi}+\Gamma(\vec{p})\,\nabla\vec{\xi})^i_j=\begin{pmatrix} \Gamma\,|\xi|\,\mathscr{K}_1 & 0 & -\Gamma\alpha_1\mathscr{K}_1 \\ 0 & \Gamma\,|\vec{\xi}|\,\mathscr{K}_2 & -\Gamma\alpha_2\mathscr{K}_2 \\ -\Gamma\alpha_1\mathscr{K}_1 & -\Gamma\alpha_2\mathscr{K}_2 & |\vec{\xi}|^2+\Gamma\dfrac{\partial^2\Gamma}{\partial(s^3)^2} \end{pmatrix} \tag{123}$$

where all quantities are evaluated at $\vec{p}_0$, i.e., $s^1=s^2=s^3=0$.

Hence in a coordinate system which has basis vectors locally parallel to the normal and appropriate tangent vectors of the $1/\Gamma$-plot the differential operator of the phase-field equation has the form

$$\begin{aligned}&\Gamma(\nabla\phi)\,\mathscr{K}_1\left[\,|\vec{\xi}|\,\frac{\partial^2\phi}{\partial(x^{\bar{1}})^2}-2\alpha_1\frac{\partial^2\phi}{\partial x^{\bar{1}}x^{\bar{3}}}\right]+\Gamma(\nabla\phi)\,\mathscr{K}_2\left[\,|\vec{\xi}|\,\frac{\partial^2\phi}{\partial(x^{\bar{2}})^2}-2\alpha_2\frac{\partial^2\phi}{\partial x^{\bar{2}}x^{\bar{3}}}\right]\\ &\qquad+\left[\frac{\partial}{\partial s^3}\left(\Gamma(\vec{p})\,\frac{\partial\Gamma(\vec{p})}{\partial s^3}\right)\right]\frac{\partial^2\phi}{\partial(x^{\bar{3}})^2}\end{aligned} \tag{124}$$

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REFERENCES

1. D. W. Hoffman and J. W. Cahn, A vector thermodynamics for anisotropic surfaces. I. Fundamentals and application to plane surface junctions, *Surf. Sci.* **31**:368–388 (1972).

2. J. W. Cahn and D. W. Hoffman, A vector thermodynamics for anisotropic surfaces. II. Curved and faceted surfaces, *Acta Metall. Mater.* **22**:1205–1214 (1974).
3. G. Wulff, *Z. Kristallog.* **34**:449 (1901).
4. *Mathematical Crystallography* (Oxford University Press, 1903).
5. F. C. Frank, The geometrical thermodynamics of surfaces, in *Metal Surfaces* (American Society of Metals, Ohio, 1962), pp. 1–16.
6. W. W. Mullins, Solid surface morphologies governed by capillarity, in *Metal Surfaces* (American Society of Metals, Ohio, 1962), pp. 17–66.
7. P. G. de Gennes, Short range order effects in the isotropic phase of nematics and cholesterics, *Mol. Cryst. Liq. Cryst.* **12**:193–214 (1971).
8. J. W. Cahn and J. E. Hilliard, Free energy of a nonuniform system. I. Interfacial free energy, *J. Chem. Phys.* **28**:258–267 (1958).
9. J. W. Cahn, On spinodal decomposition, *Acta Metall.* **9**:795–801 (1961).
10. J. W. Cahn and S. M. Allen, A microscopic theory for domain wall motion and its experimental verification in Fe-Al alloy domain growth kinetics, *J. Phys.(Paris) Colloque C7*, C7-51 (1977).
11. S. M. Allen and J. W. Cahn, A microscopic theory for antiphase boundary motion and its application to antiphase domain coarsening, *Acta metal mater.* **27**:1085–1095 (1979).
12. R. J. Braun, J. W. Cahn, G. B. McFadden and A. A. Wheeler, Anisotropy of interfaces in an ordered alloy: a multiple-order-parameter model, *Phil. Trans. Roy. Soc. London A* **355**:18331787 (1997).
13. J. S. Rowlinson and B. Widow, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1989).
14. J. E. Taylor, Mean curvature and weighted mean curvature, *Acta Metall. Mater.* **40**:1475–1485 (1992).
15. Lord Rayleigh. On the theory of surface forces.—II. Compressible fluids, *Phil. Mag.* **33**:209–220 (1892).
16. J. D. van der Waals, *Verhandel. Konink. Akad. Weten. Amsterdam (Sect. 1)*, **1**(8) (Dutch); Transl. Ostwald, 1894, Thermodynamische theorie der kapillarität unter voraussetzung stetiger dichteänderung, *Z. Phys. Chem.* **13**:657–725 (German); Transl. Anonymous, 1895, *Arch. Néerl.* **28**:121–201 (French). Transl. J. S. Rowlinson, 1979, Translation of J. D. van der Waals' "The thermodynamic theory of capillarity under the hypothesis of a continuous density variation." *J. Stat. Phys.* **20**:197–244 (From Dutch, German, French).
17. B. I. Halperin, P. C. Hohenberg, and S.-K. Ma, Renormalization-group methods for critical dynamics: I. Recursion relations and effects of energy conservation, *Phys. Rev. B* **10**:139–153 (1974).
18. J. S. Langer. Unpublished notes.
19. J. S. Langer. Models of pattern formation in first-order phase transitions, *Directions in Condensed Matter Physics*, G. Grinstein and G. Mazenko, eds. (Philadelphia, World Scientific, 1986), pp. 165–186.
20. O. Penrose and P. C. Fife, Thermodynamically consistent models of the phase-field type for the kinetics of phase transitions, *Physica D* **43**:44–62 (1990).
21. A. P. Umantsev, Thermodynamic stability of phases and transition kinetics under adiabatic conditions, *J. Chem. Phys.* **96**:605–617 (1992).
22. S.-L. Wang, R. F. Sekerka, A. A. Wheeler, B. T. Murray, S. R. Coriell, R. J. Braun, and G. B. McFadden, Thermodynamically consistent phase-field models for solidification, *Physica D* **69**:189–200, (1993).
23. P. C. Fife and O. Penrose, Interfacial dynamics for thermodynamically consistent phase-field models with nonconserved order parameter, *Electronic J. Diff. equations* **1**:1–49 (1995).

24. C. Charach and P. C. Fife, On thermodynamically consistent schemes for phase-field equations. To appear *Open Systems and Information Dynamics.*
25. S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (Dover, New York, 1984).
26. G. Caginalp and P. C. Fife. Phase-field methods for interfacial boundaries, *Phys. Rev. B* **33**:7792–7794 (1986).
27. R. Kobayashi, Modeling and numerical simulations of dendritic crystal growth, *Physica D* **63**:410–423 (1993).
28. J. E. Taylor, Mean curvature and weighted mean curvature, *Acta Metall. Mater.* **40**:1475–1485 (1992).
29. H. J. Diepers, C. Beckermann, and I. Steinbach, A phase-field method for alloy solidification with convection, in *Solidification Processing 1997*, J. Beech and H. Jones, eds., Proc. 4th Decennial Int. Conf. on Solid. Process. (University of Sheffield, Sheffield, 1997), pp. 426–430.
30. An Anisotropic Multi-phase-field Model: Interfaces and Junctions, *Phys. Rev. E.* **57**:2602–2609 (1998).
31. R. Kikuchi and J. W. Cahn, Theory of interphase and antiphase boundaries in fcc alloys, *Acta Metall.* **27**:1337–1353 (1979).
32. J. W. Cahn and R. Kikuchi, Transition layer in a lattice-gas model of a solid-liquid interface, *Phys. Rev. B* **31**:4300–4304 (1980).
33. S.-W. Lai, Theory of ordering dynamics for Cu_3Au, *Phys. Rev. B* **41**:9239–9256 (1990).
34. J. W. Cahn, S. Han and G. B. McFadden, *J. Stat. Phys.*, this issue.
35. G. Caginalp, Stefan and Hele-Shaw type models as asymptotic limits of the phase-field equation, *Phys. Rev. A* **39**:5887–5896 (1989).
36. N. Provatos, N. Goldenfeld and J. Dantzig, Efficient computation of dendritic microstructures using adaptive mesh refinement, *Phys. Rev. Lett.* **80**:3308–3311 (1998).
37. G. Caginalp and P. C. Fife, Phase-field methods for interfacial boundaries, *Phys. Rev. B* **34**:4940–4943 (1986).
38. G. Caginalp, The role of microscopic anisotropy in the macroscopic behaviour of a phase boundary, *Ann. Phys.* **172**:136–155 (1986).
39. G. B. McFadden, A. A. Wheeler, R. J. Braun, S. R. Coriell and R. F. Sekerka, Phase-field models for anisotropic interfaces, *Phys. Rev. E* **48**:2016–2024 (1993).
40. A. A. Wheeler and G. B. McFadden, A ξ-vector formulation of anisotropic phase-field models: 3D asymptotics, *Eur. J. Appl. Maths.* **7**:367–381 (1996).
41. A. A. Wheeler and G. B. McFadden, On the notion of a ξ-vector and a stress tensor for a general class of anisotropic diffuse interface models, *Proc. Roy. Soc. Lond. A* **453**:1611–1630 (1997).
42. P. C. Fife, private communication.
43. R. Courant and D. Hilbert, *Methods of Mathematical Physics*, *Volume II* (Interscience Publishers, New York, 1962).
44. D. Anderson, G. B. McFadden, and A. A. Wheeler, A phase-field model with convection. Preprint (1998).
45. D. M. Anderson, G. B. McFadden, and A. A. Wheeler, Diffuse-interface methods in fluid mechanics, *Ann. Rev. Fluid Mech.* **30**:139–165 (1998).
46. E. Fried and M. E. Gurtin, Continuum theory of thermally induced phase transitions based on an order parameters, *Physica D* **68**:326–343 (1993).
47. E. Fried and M. E. Gurtin, Dynamic solid-solid phase transitions with phase characterized by an order parameter, *Physica D* **72**:287–308 (1994).
48. M. E. Gurtin, The nature of configurational forces, *Arch. Rat. Mech. Anal.* **131**:67–100 (1995).

49. Herbert Goldstein, *Classical Mechanics* (Addison–Wesley Publishing Company, 1980).
50. D. Anderson, G. B. McFadden, and A. A. Wheeler, Unpublished notes (1998).
51. D. J. Korteweg, Sur la forme que prennent les équations du mouvements des fluides si l'on tient compte des forces capillaires causées par des variations de densité considérables mais continues et sur la théorie de la capillarité dans l'hypothèse d'une variation continue de la densité, *Arch. Néerl. Sci. Exactes Nat. Ser. II* **6**:1–24 (1901).
52. M. J. P. Musgrave, *Crystal Acoustics*; *Introduction to the Study of Waves and Vibrations in Crystals* (Holden-day, San Francisco, USA 1970).
53. F. C. Frank, in *Growth and Perfection of Crystals*, R. H. Doremus, B. W. Roberts, and D. Turnbull, eds. (Wiley, New York, 1958).
54. R. J. Braun, J. W. Cahn, G. B. McFadden, H. E. Rushmeier, and A. A. Wheeler, Theory of growth rates in the ordering of an FCC alloy, *Acta Materr.* **46**:1–12 (1998).